Table of Contents

1. Introduction
2. Classification
3. Alkanes
4. Preparation
5. Physical Properties
6. Chemical Properties
7. Conformations
8. Alkenes Structure
9. Alkenes Isomerism
10. Alkenes Preparation
11. Alkenes Physical Properties
12. Markovnikov’s and Anti-Markovnikov’s Rule
13. Dienes and Polymerization
14. Alkynes
15. Physical Properties
16. Chemical Reactions
17. Aromatic Hydrocarbons
18. Structure of Benzene
19. Huckel Rule of Aromaticity
20. Preparation of Benzene
21. Physical Properties
22. Chemical Properties
23. Directive Influence of a Functional Group in Mono-Substituted Benzene
24. Carcinogenicity and Toxicity

Introduction

Key Points

- Hydrocarbons are organic compounds made up only of carbon (C) and hydrogen (H) atoms.
- Main natural sources: natural gas, petroleum, and coal.

Solved Examples

- **Ex 1:** Identify the elements in hydrocarbons.
  Answer: Carbon and Hydrogen only.

Practice Set

- **Q1:** What elements do hydrocarbons contain?
  A. Carbon and Oxygen
  B. Carbon and Hydrogen
  C. Hydrogen and Oxygen
  D. Carbon, Hydrogen, and Oxygen
- **Q2:** Which of the following is a major source of hydrocarbons?
  A. Water
  B. Natural gas
  C. Air
  D. Salt
- **Q3:** Hydrocarbons are primarily composed of which two elements?
  A. Carbon and Nitrogen
  B. Carbon and Hydrogen
  C. Hydrogen and Oxygen
  D. Nitrogen and Oxygen

Answer Key

- **Q1:** B - Hydrocarbons contain only carbon and hydrogen atoms.

- **Q2:** B - Natural gas is a main source of hydrocarbons.
- **Q3:** B - Hydrocarbons are composed of carbon and hydrogen only.

Memory Aids

- Hydrocarbons = Hydro (H) + Carbon (C) only.
- Sources: Natural gas, Petroleum, Coal (NPC).

Classification

Types of Hydrocarbons

- Based on carbon-carbon bonds, hydrocarbons are classified into:
- **Saturated:** Only single bonds (C–C, C–H).
- **Unsaturated:** Contain double or triple bonds (C=C, C≡C).
- **Aromatic:** Special cyclic compounds with resonance (e.g., benzene).

- **Saturated Hydrocarbons:**
  - *Alkanes:* Open chain with single bonds.
  - *Cycloalkanes:* Closed ring with single bonds.
- **Unsaturated Hydrocarbons:** Contain multiple bonds (double/triple).
- **Aromatic Hydrocarbons:** Cyclic compounds with special stability due to resonance.

Solved Examples

- **Ex 1:** Classify C_2H_6.
  Answer: Saturated alkane (ethane, single bonds only).
- **Ex 2:** Classify C_2H_4.
  Answer: Unsaturated alkene (contains a double bond).

Practice Set

- **Q1:** Which hydrocarbon is saturated?
  A. Ethene
  B. Ethyne
  C. Ethane
  D. Benzene
- **Q2:** Which hydrocarbon contains a triple bond?
  A. Ethane
  B. Ethene
  C. Ethyne
  D. Cyclohexane
- **Q3:** Aromatic hydrocarbons are characterized by:
  A. Only single bonds
  B. Multiple bonds without resonance
  C. Cyclic structure with resonance
  D. Open chain with double bonds

Answer Key

- **Q1:** C - Ethane is saturated with single bonds only.
- **Q2:** C - Ethyne contains a triple bond.
- **Q3:** C - Aromatic hydrocarbons have cyclic structure with resonance.

Memory Aids

- Saturated = Single bonds only (alkanes, cycloalkanes).
- Unsaturated = Double or triple bonds (alkenes, alkynes).
- Aromatic = Cyclic with resonance (benzene ring).

Alkanes

General Properties

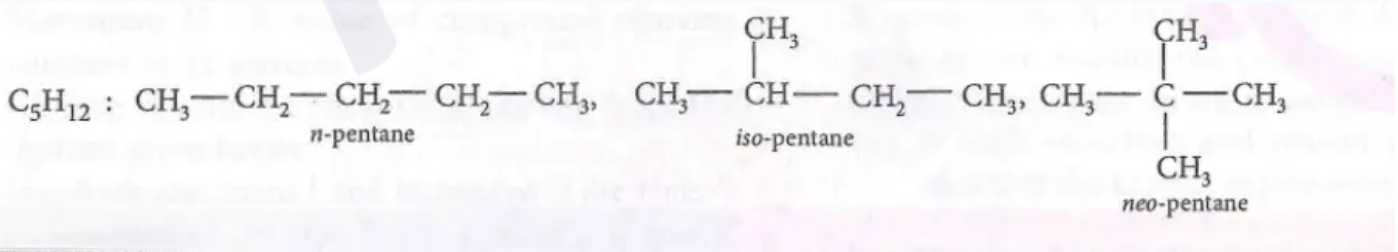
- Alkanes are saturated hydrocarbons with formula C_nH_{2n+2}.
- Examples: Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8).

Structure

- Carbon atoms are sp^3 hybridized, forming tetrahedral geometry.
- All C–C and C–H bonds are sigma (σ) bonds.
- Bond lengths: C–C = 1.54 Å, C–H = 1.09 Å; bond angle = 109° 28'.

Isomerism

- Exhibit chain isomerism.
- First three members (methane, ethane, propane) have no isomers.
- Number of isomers increases with carbon atoms: Butane (2), Pentane (3), Hexane (5), Heptane (9), Octane (18), Decane (75).



Solved Examples

- **Ex 1:** Identify isomers of pentane.
  Answer: n-pentane (straight chain), iso-pentane (one branch), neo-pentane (more branched).

Practice Set

- Q1: What is the general formula of alkanes?
  A. C_nH_{2n} B. C_nH_{2n+2} C. C_nH_{2n-2} D. C_nH_n
- Q2: Which alkane has 5 isomers?
  A. Butane B. Pentane C. Hexane D. Heptane
- Q3: What type of isomerism do alkanes exhibit?
  A. Position B. Chain C. Functional D. Geometrical

Answer Key

- Q1: B - Alkanes have the formula C_nH_{2n+2}.
- Q2: C - Hexane has 5 isomers.
- Q3: B - Alkanes show chain isomerism.

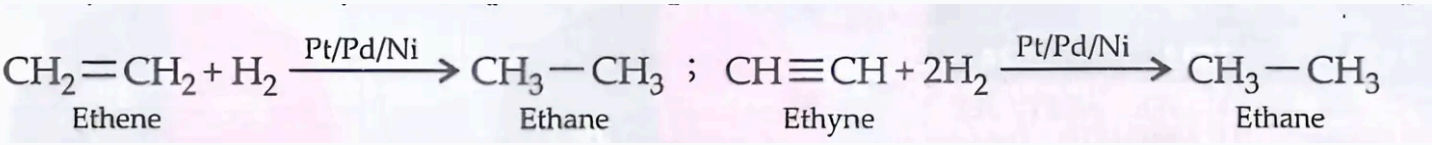
Memory Aids

- Alkanes = Saturated hydrocarbons, formula C_nH_{2n+2}.
- Isomer count increases with carbon number; no isomers for C1-C3.

Preparation

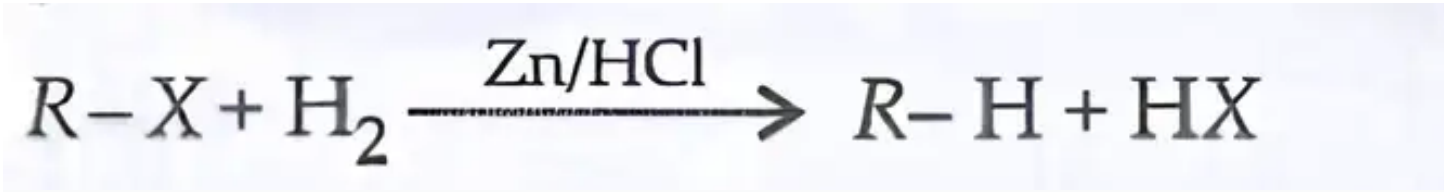
Hydrogenation of Unsaturated Hydrocarbons

- Alkenes/alkynes + H_2 (Pt, Pd, Ni catalyst) → Alkanes.



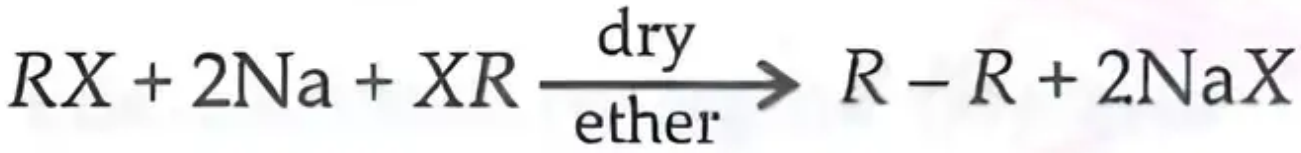
Reduction of Alkyl Halides

- Alkyl halides (except fluorides) + Zn + dilute HCl → Alkanes.



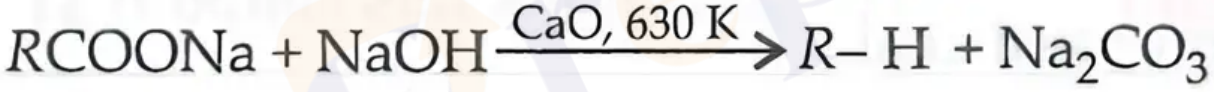
Wurtz Reaction

- Alkyl halides + 2Na (dry ether) → Higher alkanes (even carbon number) + 2NaX.

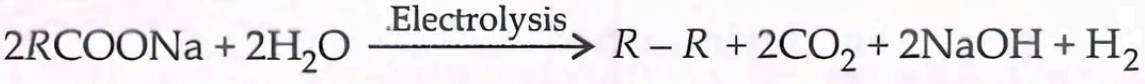


From Carboxylic Acids

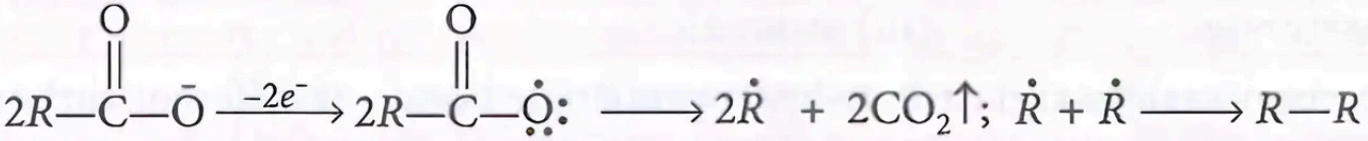
- **Decarboxylation:** Sodium salts of carboxylic acids + soda lime (NaOH + CaO) → Alkane (one C less) + CO_2.



- **Kolbe's Electrolysis:** Electrolysis of sodium/potassium salts of carboxylic acids → Alkane with even number of carbons.

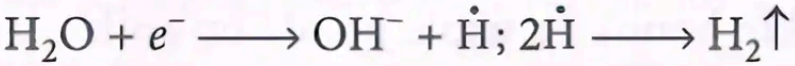


At anode :



Acetate ion — Acetate free radical — Alkyl free radical

At cathode :



Methane cannot be prepared by this method.

Solved Examples

- **Ex 1:** Write reaction for hydrogenation of ethene.
  $CH_2=CH_2 + H_2$ (Pt) → $CH_3–CH_3$
- **Ex 2:** Write Wurtz reaction for chloromethane.
  $2CH_3Cl + 2Na → C_2H_6 + 2NaCl$

Practice Set

- Q1: Which catalyst is used in hydrogenation?
  A. Fe B. Ni C. Cu D. Zn
- Q2: Wurtz reaction is used to prepare alkanes with:
  A. Odd number of carbons B. Even number of carbons C. Any number of carbons D. Only methane
- Q3: Decarboxylation removes which group?
  A. Hydroxyl B. Carboxyl C. Carbonyl D. Amino

Answer Key

- Q1: B - Nickel is a common hydrogenation catalyst.
- Q2: B - Wurtz reaction forms alkanes with even carbon numbers.
- Q3: B - Decarboxylation removes the carboxyl group.

Memory Aids

- Hydrogenation uses Pt, Pd, Ni catalysts.
- Wurtz reaction joins alkyl halides using sodium in dry ether.
- Decarboxylation removes CO_2 from carboxylic acids.

Physical Properties

States and Solubility

- C_1 to C_4: gases; C_5 to C_{17}: liquids; C_{18} and above: solids at 298 K.
- Colourless, odourless, insoluble in water, soluble in non-polar solvents.

Boiling and Melting Points

- Boiling points increase with molecular mass.
- Branching decreases boiling points.
- Alkanes with even carbon numbers have higher melting points than adjacent odd-numbered alkanes due to symmetry.

Solved Examples

- **Ex 1:** State physical state of hexane at room temperature.
  Answer: Liquid (C_5 to C_{17} are liquids).

Practice Set

- Q1: Which alkane is a gas at room temperature?
  A. Hexane B. Methane C. Octadecane D. Nonane
- Q2: Alkanes are soluble in:
  A. Water B. Polar solvents C. Non-polar solvents D. Acids
- Q3: Branching in alkanes causes:
  A. Increase in boiling point B. Decrease in boiling point C. No change D. Increase in melting point

Answer Key

- Q1: B - Methane is a gas at room temperature.
- Q2: C - Alkanes dissolve in non-polar solvents.

- Q3: B - Branching lowers boiling points.

Memory Aids

- First 4 alkanes are gases; next are liquids; long chains are solids.
- Branching lowers boiling points due to less surface contact.

Chemical Properties

Reactivity

- Generally inert to acids, bases, oxidizing and reducing agents.
- Undergo halogenation under UV light and heat.
- Halogenation rate: $F_2 > Cl_2 > Br_2 > I_2$.
- Hydrogen replacement rate: 3° > 2° > 1° hydrogens.
- Fluorination is violent; iodination is slow and reversible with oxidizing agents.

Halogenation Mechanism

- Chain initiation: UV light splits Cl_2 into 2 Cl radicals.
- Chain propagation: Cl radical abstracts H from alkane forming alkyl radical + HCl; alkyl radical reacts with Cl_2 forming alkyl halide + Cl radical.
- Chain termination: Radicals combine to form stable molecules.

- **Chain initiation step :** $Cl - Cl \xrightarrow{h\upsilon} 2\dot{C}l$
- **Chain propagation step :**

  $CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + H - Cl$; $\dot{C}H_3 + Cl - Cl \longrightarrow CH_3Cl + \dot{C}l$ ..... and so on.
- **Chain terminating step :** $\dot{C}l + \dot{C}l \longrightarrow Cl_2$; $\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$; $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$

Other Reactions

- Combustion: Complete → $CO_2 + H_2O$; Incomplete → C (soot) + H_2O.
- Controlled oxidation forms methanol, formaldehyde, ethanoic acid.
- Isomerisation converts n-butane to iso-butane.

- Aromatisation converts hexane to benzene.
- Reaction with steam produces CO and H_2.
- Pyrolysis/cracking breaks large hydrocarbons into smaller ones.

Solved Examples

- **Ex 1:** Write the product of methane chlorination.
  $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (under UV light)

Practice Set

- Q1: Which halogen reacts fastest with alkanes?
  A. I_2 B. Br_2 C. Cl_2 D. F_2
- Q2: Rate of hydrogen replacement in alkanes is:
  A. 1° > 2° > 3° B. 3° > 2° > 1° C. 2° > 3° > 1° D. Equal for all
- Q3: What is the main step in chain propagation during halogenation?
  A. Radical formation B. Radical combination C. Hydrogen abstraction D. Radical termination

Answer Key

- Q1: D - Fluorine reacts fastest but is violent.
- Q2: B - Tertiary hydrogens are replaced fastest.
- Q3: C - Hydrogen abstraction by halogen radical is key propagation step.

Memory Aids

- Halogenation proceeds via free radical mechanism: initiation, propagation, termination.
- Fluorination is uncontrollable; iodination is slow and reversible.
- Substitution rate: 3° > 2° > 1° hydrogens.

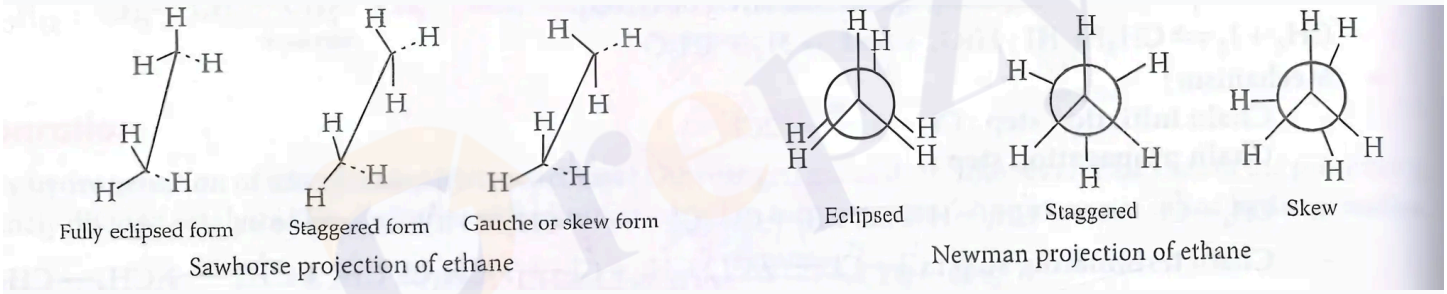
Conformations

Definition

- Conformational isomers arise from rotation about C–C single bonds.
- Also called rotational isomers.

Conformations of Ethane

- Infinite conformations possible by rotation of one methyl group around C–C bond.
- **Eclipsed:** Hydrogens align, causing maximum repulsion; least stable.
- **Staggered:** Hydrogens are maximally apart; most stable, 12.5 kJ/mol more stable than eclipsed.
- **Skew (Gauche):** Intermediate conformations between eclipsed and staggered.



Solved Examples

- **Ex 1:** Identify the most stable conformation of ethane.
  Answer: Staggered conformation.

Practice Set

- Q1: Which conformation has highest energy?
  A. Staggered B. Eclipsed C. Skew D. Chair
- Q2: Rotation about which bond causes conformational isomerism?
  A. C=O B. C–C single bond C. C≡C D. C–H
- Q3: Energy difference between eclipsed and staggered ethane is approximately:
  A. 5 kJ/mol B. 12.5 kJ/mol C. 20 kJ/mol D. 50 kJ/mol

Answer Key

- Q1: B - Eclipsed conformation has highest energy due to repulsion.
- Q2: B - Rotation about C–C single bond causes conformational isomerism.
- Q3: B - Energy difference is about 12.5 kJ/mol.

Memory Aids

- Staggered = stable; eclipsed = unstable; skew = intermediate.
- Rotation about C–C single bond changes conformation.

Alkenes Structure

Explanation

- Alkenes have molecular formula C_nH_{2n} with a carbon-carbon double bond (C=C).
- In ethylene, sp^2 orbitals of carbons overlap axially forming a sigma (σ) bond.
- Remaining sp^2 orbitals overlap with hydrogen 1s orbitals.
- Pure p orbitals on carbons overlap sideways forming a pi (π) bond.
- Double bond consists of one σ and one π bond.

Solved Examples

- **Ex 1:** Describe bonding in ethene.
  - Each carbon is sp^2 hybridized.
  - σ bond formed by axial overlap of sp^2 orbitals.
  - π bond formed by lateral overlap of p orbitals.

Practice Set

- Q1: What type of hybridization is present in alkene carbons?
  - A. sp

    - B. sp^2
    - C. sp^3
    - D. dsp^2
- Q2: The pi bond in alkenes is formed by overlap of?
    - A. sp^2 orbitals
    - B. p orbitals
    - C. s orbitals
    - D. sp orbitals
- Q3: Which bond in alkene allows free rotation?
    - A. Sigma bond
    - B. Pi bond
    - C. Both sigma and pi bonds
    - D. None

Answer Key

- Q1: B - Alkene carbons are sp^2 hybridized.
- Q2: B - Pi bond is formed by lateral overlap of p orbitals.
- Q3: A - Sigma bond allows free rotation; pi bond restricts rotation.

Memory Aids

- Double bond = 1 σ + 1 π bond.
- sp^2 hybridization in alkene carbons.
- Pi bond formed by sideways p orbital overlap.

Alkenes Isomerism

Explanation

- **Chain isomerism:** Different carbon chain arrangements (e.g., 1-pentene and 2-methyl-1-butene).
- **Position isomerism:** Double bond position differs (e.g., 1-butene vs 2-butene).

- **Ring chain isomerism:** One is open chain, other is cyclic (e.g., propene and cyclopropane).
- **Geometrical isomerism:** Due to restricted rotation around C=C, cis (same side) and trans (opposite side) forms exist.
- Trans isomers are generally more stable than cis due to less steric crowding.

Solved Examples

- **Ex 1:** Identify isomers of butene.
  - 1-butene: double bond at carbon 1.
  - 2-butene: double bond at carbon 2 (cis and trans forms).

Practice Set

- Q1: Which is an example of chain isomerism?
  - A. 1-butene and 2-butene
  - B. 1-pentene and 2-methyl-1-butene
  - C. Cis-butene and trans-butene
  - D. Propene and cyclopropane
- Q2: Geometrical isomerism arises due to?
  - A. Free rotation around C=C
  - B. Restricted rotation around C=C
  - C. Different molecular formula
  - D. Different carbon chain
- Q3: Which is more stable?
  - A. Cis-isomer
  - B. Trans-isomer
  - C. Both equally stable
  - D. None

Answer Key

- Q1: B - Chain isomerism involves different carbon chains.
- Q2: B - Geometrical isomerism due to restricted rotation around double bond.
- Q3: B - Trans isomers are more stable due to less steric hindrance.

Memory Aids

- Cis = same side; Trans = opposite side.
- Chain isomers differ in carbon skeleton.
- Position isomers differ in double bond location.

Alkenes Preparation

Explanation

- **Partial hydrogenation of alkynes:** Using Lindlar's catalyst (Pd on $CaCO_3$ poisoned with Pb), alkynes convert to cis-alkenes.
- **Birch reduction:** Sodium in liquid ammonia converts alkynes to trans-alkenes.
- **Dehydrohalogenation of alkyl halides:** β-elimination using alcoholic KOH removes HX forming alkenes.
- **From vicinal dihalides:** Zn reduces vicinal dihalides to alkenes.
- **Dehydration of alcohols:** Heating alcohols with conc. H_2SO_4 removes water forming alkenes.
- **Saytzeff rule:** More substituted alkene is major product.

Solved Examples

- **Ex 1:** Partial hydrogenation of ethyne.
  - $C_2H_2 + H_2$ (Lindlar's catalyst) → C_2H_4 (cis-ethene)
- **Ex 2:** Dehydrohalogenation of 1-bromoethane.
  - $CH_3CH_2Br + KOH$ (alc) → $CH_2{=}CH_2 + KBr + H_2O$

Practice Set

- Q1: Lindlar's catalyst produces which alkene?
  - A. Trans-alkene
  - B. Cis-alkene
  - C. Alkane

    - D. Alkyne
- Q2: Dehydration of alcohols requires?
    - A. Dilute H_2SO_4
    - B. Conc. H_2SO_4 and heat
    - C. KOH and heat
    - D. Na and NH_3
- Q3: In dehydrohalogenation, which carbon loses hydrogen?
    - A. α-carbon
    - B. β-carbon
    - C. γ-carbon
    - D. None

Answer Key

- Q1: B - Lindlar's catalyst gives cis-alkenes.
- Q2: B - Dehydration requires conc. H_2SO_4 and heat.
- Q3: B - Hydrogen is removed from β-carbon in dehydrohalogenation.

Memory Aids

- Lindlar's catalyst → cis-alkene.
- Birch reduction → trans-alkene.
- Saytzeff rule → more substituted alkene major product.

Alkenes Physical Properties

Explanation

- First 3 alkenes are gases; next 14 are liquids; higher are solids.
- All alkenes are colourless and odourless except ethene (faint sweet smell).
- Insoluble in water; soluble in non-polar solvents.
- Boiling points increase with molecular size; straight chains have higher boiling points than branched isomers.

Solved Examples

- **Ex 1:** Boiling point trend.
  - Butene (C_4H_8) boiling point higher than 2-methylpropene due to straight chain.

Practice Set

- Q1: Which alkene is a gas at room temperature?
  - A. Ethene
  - B. Hexene
  - C. Decene
  - D. Dodecene
- Q2: Alkenes are generally soluble in?
  - A. Water
  - B. Polar solvents
  - C. Non-polar solvents
  - D. None
- Q3: Boiling point increases with?
  - A. Branching
  - B. Molecular size
  - C. Decrease in chain length
  - D. None

Answer Key

- Q1: A - First three alkenes including ethene are gases.
- Q2: C - Alkenes dissolve in non-polar solvents.
- Q3: B - Boiling point increases with molecular size.

Memory Aids

- Alkenes: gases (C1-C3), liquids (C4-C17), solids (higher).
- Insoluble in water, soluble in non-polar solvents.
- Straight chain > branched in boiling point.

Markovnikov’s and Anti-Markovnikov’s Rule

Explanation

- Markovnikov’s rule: In addition to unsymmetrical alkenes, the negative part of the reagent attaches to carbon with fewer hydrogens.
- Anti-Markovnikov’s rule (Peroxide effect): In presence of peroxide, HBr adds opposite to Markovnikov’s rule.
- Peroxide effect observed only with HBr, not HCl or HI.

Solved Examples

- **Ex 1:** Addition of HBr to propene.
  - Without peroxide: Br attaches to carbon with fewer H (Markovnikov product).
  - With peroxide: Br attaches to carbon with more H (Anti-Markovnikov product).

Practice Set

- Q1: Markovnikov’s rule applies to addition of?
  - A. HCl
  - B. HBr without peroxide
  - C. HBr with peroxide
  - D. HI
- Q2: Anti-Markovnikov addition occurs in presence of?
  - A. Heat
  - B. Peroxide
  - C. Acid
  - D. Base
- Q3: Peroxide effect is observed with?
  - A. HCl
  - B. HBr
  - C. HI
  - D. All HX

Answer Key

- Q1: B - Markovnikov’s rule applies to HBr without peroxide.
- Q2: B - Peroxide causes Anti-Markovnikov addition.
- Q3: B - Peroxide effect only with HBr.

Memory Aids

- Markovnikov: Negative part attaches to carbon with fewer H.
- Anti-Markovnikov: Peroxide reverses addition in HBr.
- Peroxide effect only with HBr.

Dienes and Polymerization

Explanation

- Dienes: Alkenes with two double bonds.
- Types of dienes:
  - Isolated dienes: double bonds separated by ≥1 single bond.
  - Conjugated dienes: double bonds separated by exactly one single bond.
  - Cumulated dienes: double bonds adjacent on same carbon.
- Polymerization: Alkenes like propene polymerize under heat, pressure, and catalyst to form polymers (e.g., polypropylene).
- Polymer structure: Repeating units with opened double bonds linked in chains.

Solved Examples

- **Ex 1:** Polymerization of propene.
  - Many propene molecules (CH_3-CH=CH_2) link to form polypropylene.
  - Requires heat, pressure, and catalyst.

Practice Set

- Q1: Dienes have how many double bonds?
  - A. One
  - B. Two
  - C. Three
  - D. None
- Q2: Conjugated dienes have double bonds separated by?
  - A. No bond
  - B. One single bond
  - C. Two single bonds
  - D. Adjacent carbons
- Q3: Polymerization of propene produces?
  - A. Polyethylene
  - B. Polypropylene
  - C. Polystyrene
  - D. Polyvinyl chloride

Answer Key

- Q1: B - Dienes have two double bonds.
- Q2: B - Conjugated dienes have double bonds separated by one single bond.
- Q3: B - Propene polymerizes to polypropylene.

Memory Aids

- Dienes = 2 double bonds.
- Conjugated = alternate double bonds.
- Polymerization opens double bonds to form chains.

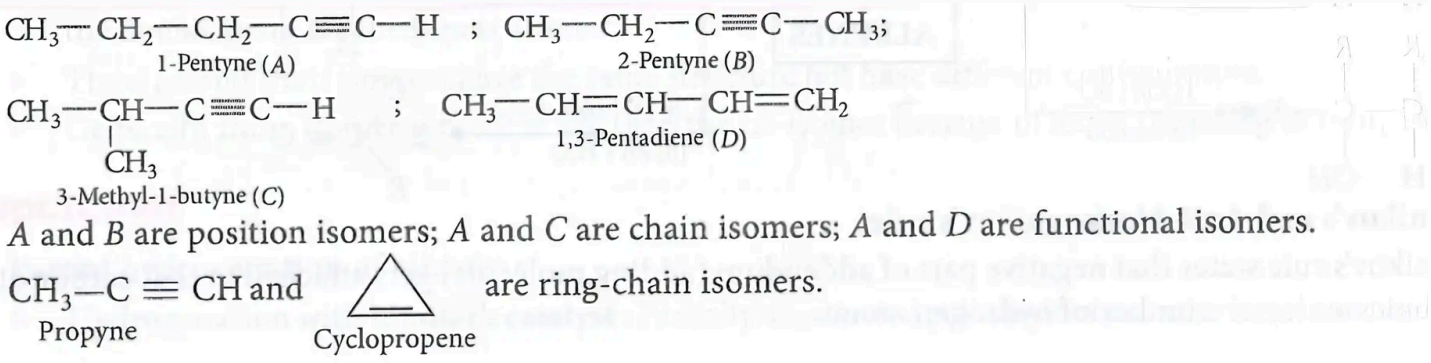
Alkynes

Definition and Characteristics

- Alkynes are unsaturated hydrocarbons with the general formula C_nH_{2n-2}.
- Contain a carbon-carbon triple bond (≡), e.g., acetylene (C_2H_2, HC≡CH) and propyne ($HC{\equiv}CCH_3$).
- More acidic than alkenes and alkanes due to sp-hybridised carbon atoms which are more electronegative.

Isomerism

- Ethyne does not show isomerism.
- Other alkynes exhibit chain, position, and functional isomerism.
- Examples include:
  - Position isomers: 1-Pentyne and 2-Pentyne (same chain, different triple bond position).
  - Chain isomers: 1-Pentyne and 3-Methyl-1-butyne (different carbon chain arrangement).
  - Functional isomers: 1-Pentyne and 1,3-Pentadiene (alkyne vs diene).
  - Ring-chain isomers: Propyne (linear) and cyclopropene (ring) with same formula but different structures.



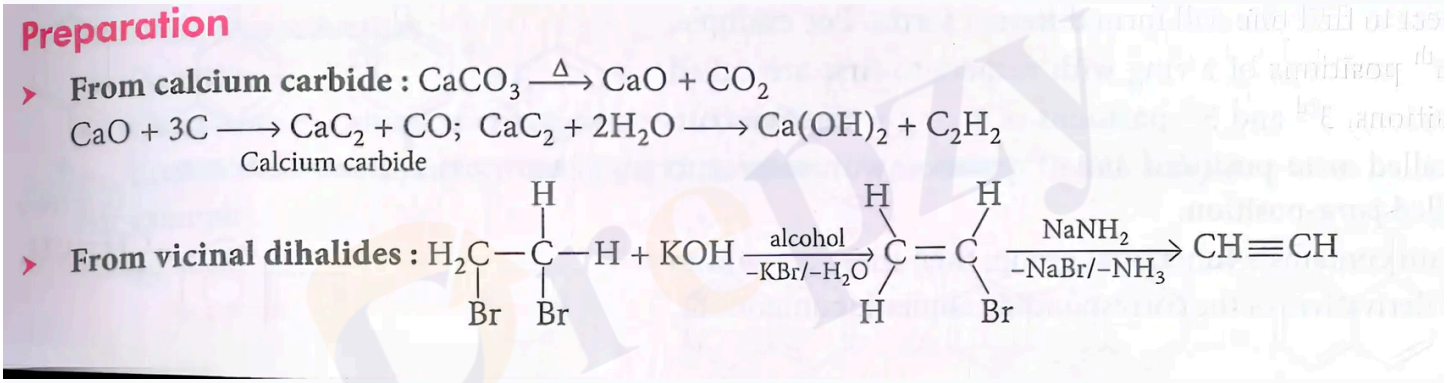
Structure

- In acetylene, sp-hybridised orbitals of carbons overlap axially to form a C–C σ-bond.

- Each carbon's other sp orbital overlaps with hydrogen 1s orbitals forming two C–H σ-bonds.
- Remaining p-orbitals overlap sideways forming two C–C π-bonds.

Preparation of Acetylene

- From calcium carbide:
  - Heat $CaCO_3 \rightarrow CaO + CO_2$
  - $CaO + C \rightarrow CaC_2$
  - $CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$
- From vicinal dihalides:
  - Vicinal dihalide + alcoholic KOH → alkene
  - Alkene + $NaNH_2$ → acetylene (C_2H_2)



Solved Examples

- **Ex 1:** Write the reaction for acetylene preparation from calcium carbide.
  - $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

Practice Set

- Q1: What is the general formula of alkynes?
  - A. C_nH_{2n+2}
  - B. C_nH_{2n}
  - C. C_nH_{2n-2}
  - D. C_nH_n
- Q2: Which type of isomerism is not shown by ethyne?

    - A. Chain isomerism
    - B. Position isomerism
    - C. Functional isomerism
    - D. All of the above
- Q3: Which compound is a ring-chain isomer of propyne?
    - A. 1-Pentyne
    - B. Cyclopropene
    - C. 1,3-Pentadiene
    - D. 3-Methyl-1-butyne

Answer Key

- Q1: C - Alkynes have the formula C_nH_{2n-2} due to one triple bond.
- Q2: D - Ethyne does not show chain, position, or functional isomerism.
- Q3: B - Cyclopropene is a ring-chain isomer of propyne (same formula, different structure).

Memory Aids

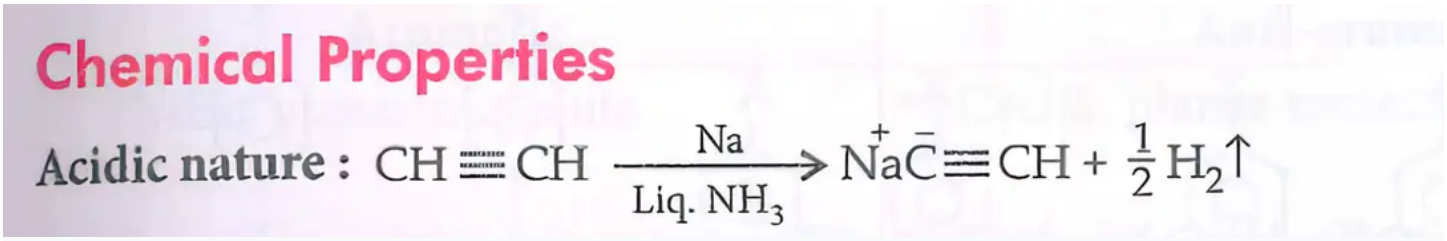
- Alkynes = C_nH_{2n-2}, triple bond present.
- Ethyne = no isomers; others show chain, position, functional isomers.
- Ring-chain isomers: linear alkynes vs cyclic alkenes.

Physical Properties

General Properties

- First three alkynes are gases; next eight are liquids; higher members are solids.
- All alkynes are colourless and odourless except ethyne which has a characteristic odour.
- Insoluble in water; soluble in non-polar solvents.
- Melting point, boiling point, and density increase with molar mass.

Chemical Properties



Acidic Nature

- Acetylene reacts with sodium in liquid ammonia to form sodium acetylide and hydrogen gas:
  - $CH{\equiv}CH + 2Na \rightarrow 2NaC{\equiv}CH + H_2$
- Acidic character order: $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$.
- —C≡CH group is acidic due to 50% s-character of sp-hybridised carbon, facilitating proton release.

Solved Examples

- **Ex 1:** Write the reaction of acetylene with sodium in liquid ammonia.
  - $CH{\equiv}CH + 2Na \rightarrow 2NaC{\equiv}CH + H_2$

Practice Set

- Q1: Which alkyne member is a gas at room temperature?
  - A. C_5H_8
  - B. C_2H_2
  - C. $C_{10}H_{18}$
  - D. $C_{12}H_{22}$
- Q2: Why are alkynes more acidic than alkenes?
  - A. Due to sp^3 hybridisation
  - B. Due to sp^2 hybridisation
  - C. Due to sp hybridisation with higher s-character
  - D. Due to presence of double bond
- Q3: What is the product when acetylene reacts with sodium in liquid ammonia?
  - A. Sodium ethoxide
  - B. Sodium acetylide
  - C. Sodium hydroxide

- D. Sodium chloride

Answer Key

- Q1: B - First three alkynes including acetylene (C_2H_2) are gases.
- Q2: C - sp hybridisation has 50% s-character, increasing acidity.
- Q3: B - Acetylene reacts with sodium to form sodium acetylide.

Memory Aids

- Acidity order: alkyne > alkene > alkane.
- sp hybridised carbons increase acidity due to higher s-character.
- Acetylene + Na → sodium acetylide + H_2.

Chemical Reactions

Addition Reactions

- Hydrogenation:
  - $C_2H_2 + H_2$ (Ni, heat) → C_2H_4 → C_2H_6
- Halogenation:
  - $C_2H_2 + Cl_2$ (CCl_4) → addition of Cl atoms
  - C_2H_2 + HBr → stepwise addition of Br atoms
- Hydration:
  - $C_2H_2 + H_2O + H_2SO_4$ ($HgSO_4$) → acetaldehyde (via tautomerism)

Polymerisation

- Linear polymerisation: multiple acetylene molecules form polyacetylene (polyethyne).
- Cyclic polymerisation: 3 acetylene molecules react in hot iron tube to form benzene.

- **Addition reactions :** $CH \equiv CH \xrightarrow[523\text{-}573\ K]{Ni,H_2} \underset{CH_2}{\overset{CH_2}{\|}} \xrightarrow{H_2} \underset{CH_3}{\overset{CH_3}{|}}$

  $CH \equiv CH \xrightarrow{Cl_2/CCl_4} \underset{CHCl}{\overset{CHCl}{\|}} \xrightarrow{Cl_2/CCl_4} \underset{CHCl_2}{\overset{CHCl_2}{|}}$; $CH \equiv CH \xrightarrow{HBr} \underset{CHBr}{\overset{CH_2}{\|}} \xrightarrow{HBr} \underset{CHBr_2}{\overset{CH_3}{|}}$

  $CH \equiv CH \xrightarrow[HgSO_4,\ 333\ K]{H_2O,\ H_2SO_4} \underset{CHOH}{\overset{CH_2}{\|}} \xrightarrow{Tautomerises} CH_3CHO$
- **Linear polymerisation :** $nCH \equiv CH \longrightarrow \underset{\text{Polyacetylene or polyethyne}}{+CH=CH-CH=CH+_n}$
- **Cyclic polymerisation :** $3HC \equiv CH \xrightarrow[873\ K]{\text{red hot Fe tube}}$ 

Solved Examples

- **Ex 1:** Write the product of acetylene hydrogenation.
  - $C_2H_2 + 2H_2$ (Ni) → C_2H_6

Practice Set

- Q1: What is the product of acetylene hydrogenation?
  - A. Ethylene
  - B. Ethane
  - C. Ethanol
  - D. Acetaldehyde
- Q2: Which catalyst is used for acetylene hydration?
  - A. Nickel
  - B. Mercury sulfate
  - C. Platinum
  - D. Iron
- Q3: What is formed by cyclic polymerisation of acetylene?
  - A. Polyacetylene
  - B. Benzene
  - C. Ethane
  - D. Cyclohexane

Answer Key

- Q1: B - Acetylene hydrogenates to ethane with Ni catalyst.
- Q2: B - $HgSO_4$ catalyses hydration to acetaldehyde.
- Q3: B - Cyclic polymerisation forms benzene.

Memory Aids

- Hydrogenation: acetylene → ethylene → ethane (Ni catalyst).
- Hydration uses $HgSO_4$ catalyst to form acetaldehyde.
- 3 acetylene molecules → benzene (cyclic polymerisation).

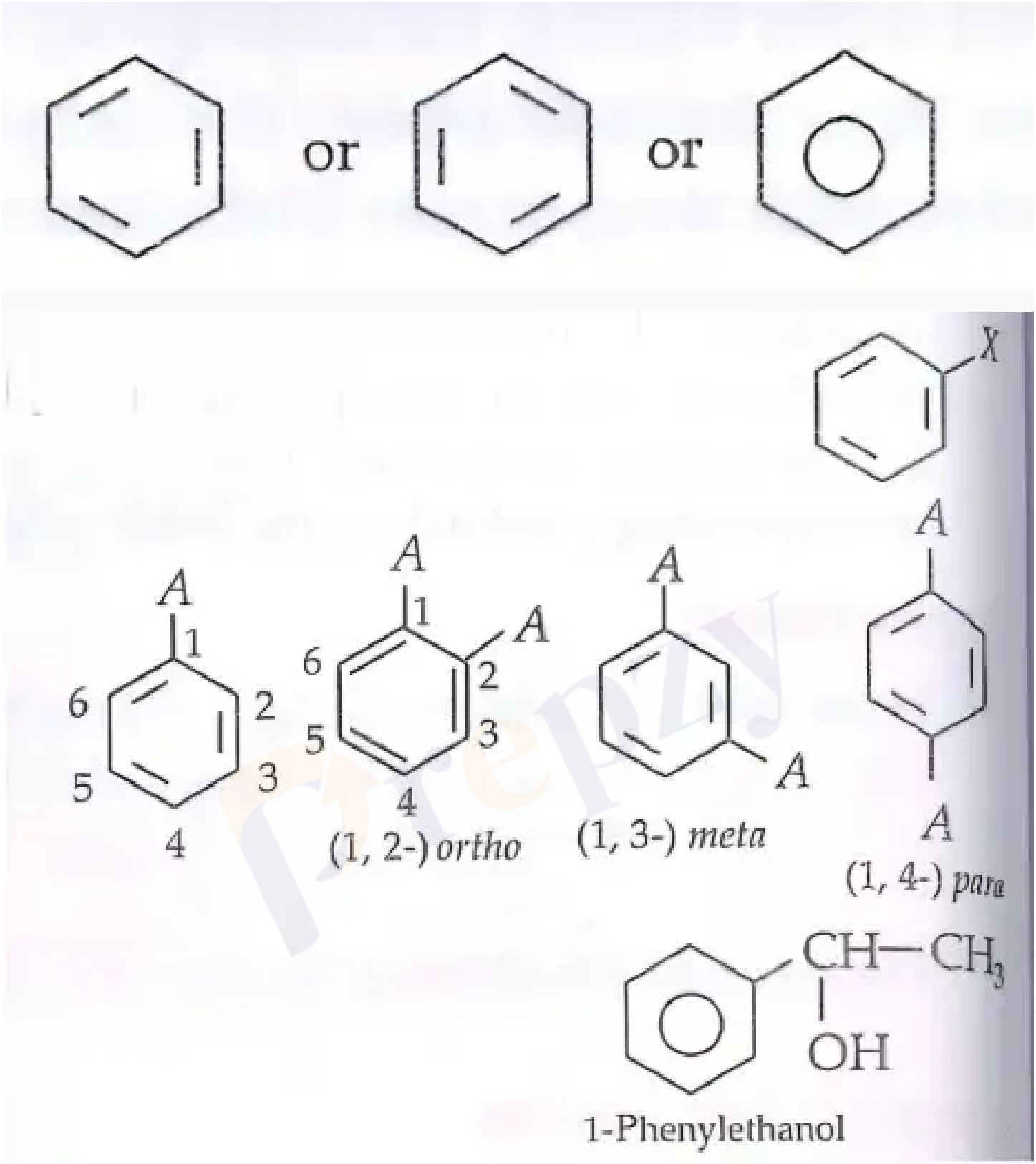
Aromatic Hydrocarbons

Overview

- Aromatic hydrocarbons are called arenes; benzene is the simplest arene.
- General formula: C_nH_{2n-6m}, where $n \geq 6$, m = number of benzene rings.

Nomenclature

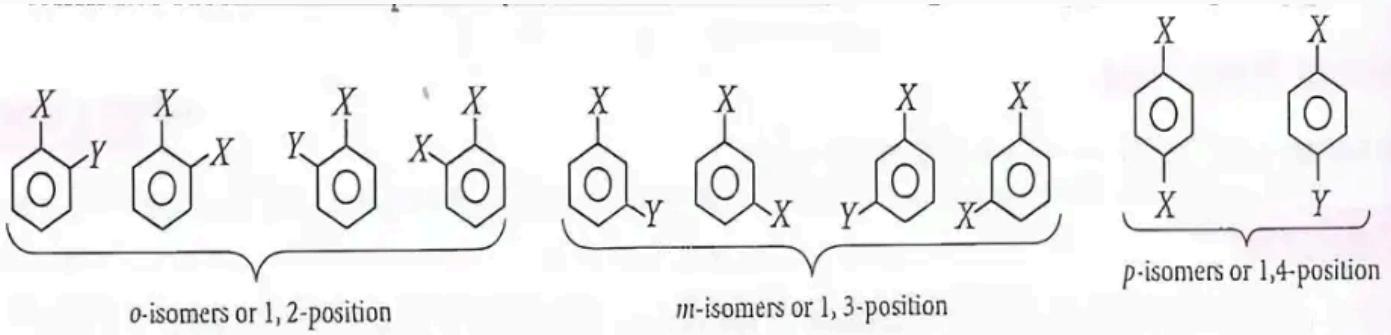
- Aromatic compounds consist of nucleus (benzene ring) and side chain (alkyl or aliphatic groups attached).
- Benzene ring carbons are sp^2 hybridised with alternating double bonds or delocalised π-electrons.
- Monosubstituted derivatives: one hydrogen replaced by alkyl/group.
- Disubstituted derivatives: substituents at ortho (1,2), meta (1,3), para (1,4) positions.
- Phenyl derivatives: side chains with functional groups attached to benzene.

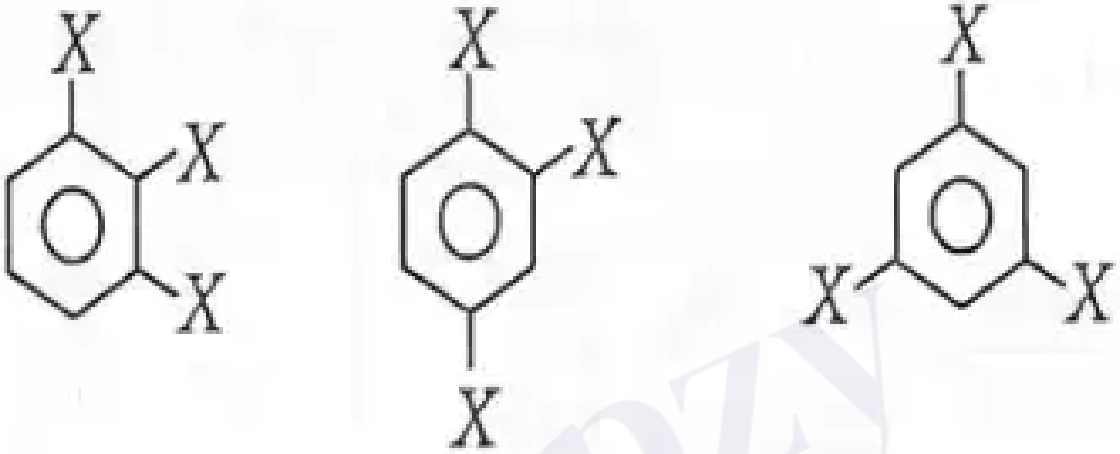


Isomerism

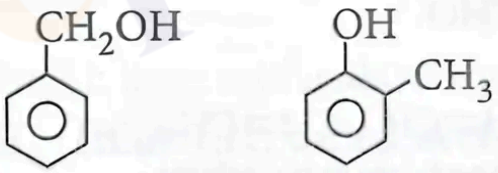
- All six hydrogens in benzene are equivalent; only one monosubstituted derivative possible.
- Position isomerism: two substituents form ortho, meta, para isomers.
- Three identical substituents yield three position isomers.
- Two same and one different substituent: six isomers; all different: ten isomers.

- Functional isomerism: e.g., benzyl alcohol and o-cresol (same formula, different structure).
- Tautomerism: keto-enol isomerism in acetophenone due to α-hydrogen mobility.

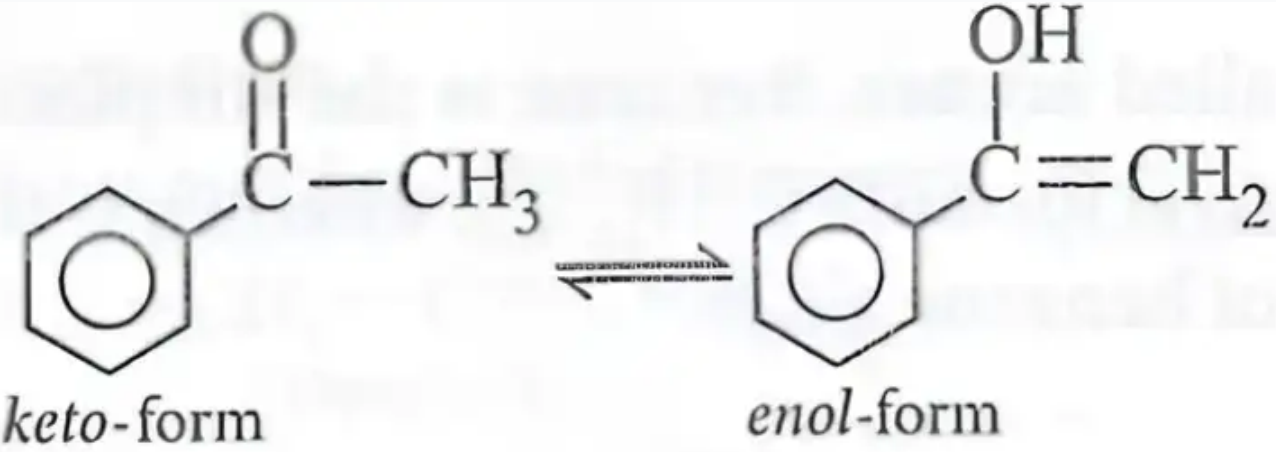




Molecular formula = C_7H_8O :



Benzyl alcohol *o*-Cresol



keto-form *enol*-form

Solved Examples

- **Ex 1:** Identify the type of isomerism in benzyl alcohol and o-cresol.
  Solution: Functional isomerism due to different functional groups ($-CH_2OH$ vs $-OH$).
- **Ex 2:** How many position isomers are possible for disubstituted benzene?
  Solution: Three (ortho, meta, para).

Practice Set

- Q1: What is the general formula of arenes?
  A. C_nH_{2n} B. C_nH_{2n-6m} C. C_nH_{2n+6} D. C_nH_n
- Q2: Which positions are called meta in disubstituted benzene?
  A. 1,2 B. 1,3 C. 1,4 D. 2,4
- Q3: How many isomers are possible when two substituents are same and one is different?
  A. 3 B. 6 C. 9 D. 10

Answer Key

- Q1: B - Arenes follow C_nH_{2n-6m} formula.
- Q2: B - Meta positions are 1,3.
- Q3: B - Six isomers possible with two same and one different substituent.

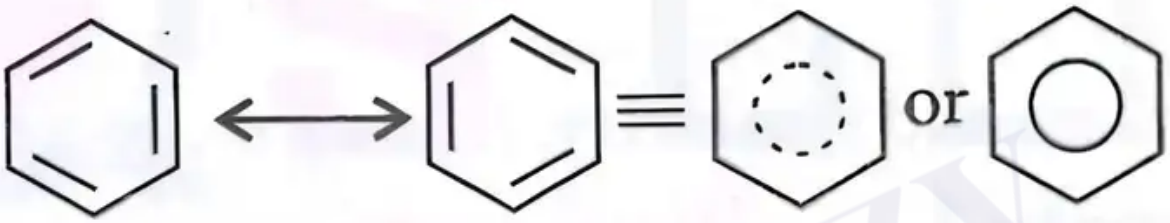
Memory Aids

- Ortho = adjacent carbons (1,2), Meta = separated by one carbon (1,3), Para = opposite carbons (1,4).
- Functional isomers have same formula but different functional groups.
- Tautomerism involves keto-enol interconversion.

Structure of Benzene

Bonding and Hybridisation

- Each carbon is sp^2 hybridised.
- Two sp^2 orbitals form σ bonds with adjacent carbons; third forms σ bond with hydrogen.
- Unhybridised p-orbitals overlap to form delocalised π-electrons above and below the ring plane.
- All bonds lie in the same plane.
- High unsaturation and unusual stability due to resonance.



Solved Examples

- **Ex 1:** Explain why benzene is more stable than cyclohexatriene.
  Solution: Resonance delocalisation of π-electrons in benzene stabilises it.

Practice Set

- Q1: What is the hybridisation of carbon atoms in benzene?
  A. sp B. sp^2 C. sp^3 D. sp^2d
- Q2: What type of bond forms between carbon and hydrogen in benzene?
  A. π bond B. σ bond C. Ionic bond D. Hydrogen bond
- Q3: Why is benzene unusually stable?
  A. Due to single bonds B. Due to resonance C. Due to ionic bonds D. Due to hydrogen bonding

Answer Key

- Q1: B - Carbon atoms in benzene are sp^2 hybridised.
- Q2: B - σ bonds form between carbon and hydrogen.
- Q3: B - Resonance delocalisation provides stability.

Memory Aids

- Benzene ring is planar with delocalised π-electrons.
- Resonance structures show bond equalisation.

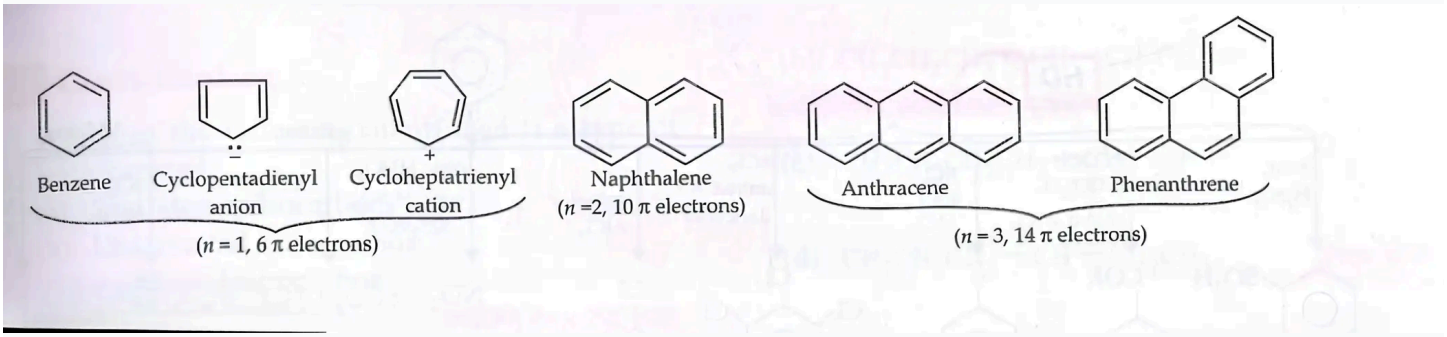
Huckel Rule of Aromaticity

Criteria for Aromaticity

- Ring must be planar.
- Complete delocalisation of π-electrons in the ring.
- Number of π-electrons must be (4n + 2), where n = 0,1,2,...

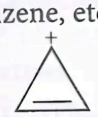
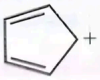
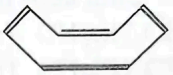
Examples

- Benzene (6 π-electrons, n=1) is aromatic.
- Cyclopentadienyl anion and cycloheptatrienyl cation (6 π-electrons) are aromatic.
- Naphthalene (10 π-electrons, n=2) and anthracene/phenanthrene (14 π-electrons, n=3) are aromatic.



Comparison of Aromatic, Anti-aromatic and Non-aromatic

- **Aromatic:** Cyclic, planar, delocalised π-electrons, follow (4n+2) rule, e.g., benzene.
- **Anti-aromatic:** Cyclic, planar, delocalised π-electrons, follow 4n rule, e.g., cyclopentadienyl cation.
- **Non-aromatic:** Non-planar or non-cyclic, no delocalisation, e.g., cyclooctatetraene.

Aromatic	Anti-aromatic	Non-aromatic
• Cyclic, planar molecule • Complete delocalisation of π electrons • Follow Huckel's rule $(4n + 2)\ \pi e^{-}s$ • *e.g.*, cycloheptatrienyl cation (tropylium ion), cyclopropenyl cation, benzene, etc.  Cyclopropenyl cation (Aromatic)	• Cyclic, planar molecule • Complete delocalisation of π-electrons • Follow $4n\ \pi e^{-}s$ • *e.g.*, cyclopentadienyl cation, cyclopropenyl anion, etc.  Cyclopentadienyl cation (Anti-aromatic)  Cyclopropenyl anion (Anti-aromatic)	• Either non-cyclic or non-planar • No delocalisation of π electrons. • May or may not follow Huckel's rule. • *e.g.*, cyclooctatetraene (tub-shaped), etc.  Cyclooctatetraene (Non-aromatic)

Solved Examples

- **Ex 1:** Determine if cyclopentadienyl anion is aromatic.
  Solution: It has 6 π-electrons (4n+2, n=1), planar and cyclic, so aromatic.

Practice Set

- Q1: What is the number of π-electrons in benzene?
  A. 4 B. 6 C. 8 D. 10
- Q2: Which rule defines aromaticity?
  A. (4n) B. (4n+2) C. (2n+1) D. (3n+2)
- Q3: Which molecule is anti-aromatic?
  A. Benzene B. Cyclopentadienyl cation C. Naphthalene D. Anthracene

Answer Key

- Q1: B - Benzene has 6 π-electrons.
- Q2: B - Huckel's rule is (4n+2) π-electrons.
- Q3: B - Cyclopentadienyl cation follows 4n rule, anti-aromatic.

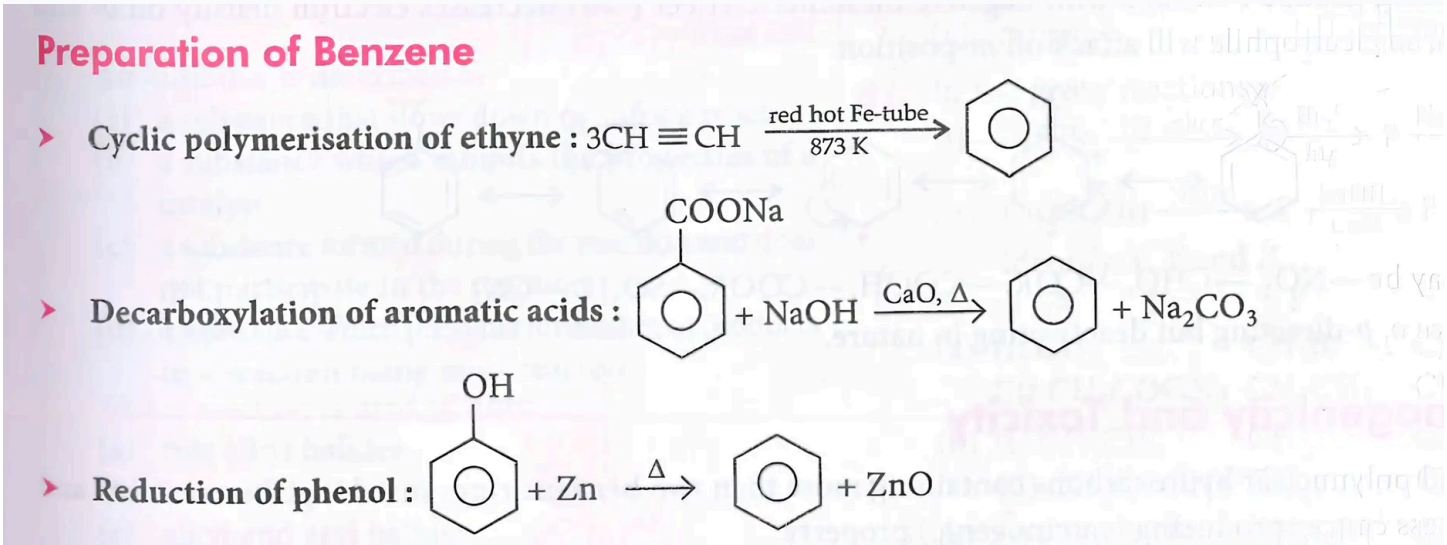
Memory Aids

- Aromatic: planar, cyclic, (4n+2) π-electrons.
- Anti-aromatic: planar, cyclic, 4n π-electrons.
- Non-aromatic: non-planar or non-cyclic.

Preparation of Benzene

Methods

- Cyclic polymerisation of ethyne: 3 CH≡CH molecules heated at 873 K in red-hot iron tube form benzene.
- Decarboxylation of aromatic acids: Benzene carboxylate salt + NaOH + CaO heat → benzene + CO_2 + Na_2CO_3.
- Reduction of phenol: Phenol + Zn heat → benzene + ZnO.



Solved Examples

- **Ex 1:** Write the reaction for benzene preparation by decarboxylation.
  Solution: $C_6H_5COONa + NaOH + CaO \rightarrow C_6H_6 + Na_2CO_3 + CO_2$.

Practice Set

- Q1: Which reagent is used in cyclic polymerisation of ethyne?
  A. Zn B. CaO C. Red-hot iron tube D. NaOH
- Q2: What is the product of phenol reduction with zinc?
  A. Cyclohexane B. Benzene C. Phenol D. Benzene oxide
- Q3: Decarboxylation of benzoic acid salt produces?
  A. Toluene B. Benzene C. Phenol D. Benzaldehyde

Answer Key

- Q1: C - Red-hot iron tube is used for ethyne polymerisation.
- Q2: B - Phenol reduces to benzene with zinc.
- Q3: B - Decarboxylation yields benzene.

Memory Aids

- Ethynes polymerise at high temperature to benzene.
- Decarboxylation removes CO_2 from aromatic acid salts.
- Phenol reduction with Zn yields benzene.

Physical Properties

Key Points

- Aromatic hydrocarbons are non-polar.
- Colourless liquids or solids with characteristic aroma.
- Immiscible with water, miscible with organic solvents.

- Burn with sooty flame.
- Boiling point increases with molecular size due to van der Waals forces.
- Melting point depends on size and symmetry; p-isomer of xylenes has highest melting point.

Solved Examples

- **Ex 1:** Why does boiling point increase with molecular size?
  Solution: Increased van der Waals forces with larger molecules.

Practice Set

- Q1: Aromatic hydrocarbons are generally:
  A. Polar B. Non-polar C. Ionic D. Metallic
- Q2: Which is miscible with water?
  A. Benzene B. Ethanol C. Toluene D. Xylene
- Q3: Which isomer of xylene has highest melting point?
  A. Ortho B. Meta C. Para D. None

Answer Key

- Q1: B - Aromatic hydrocarbons are non-polar.
- Q2: B - Ethanol is miscible with water, arenes are not.
- Q3: C - Para-xylene has highest melting point due to symmetry.

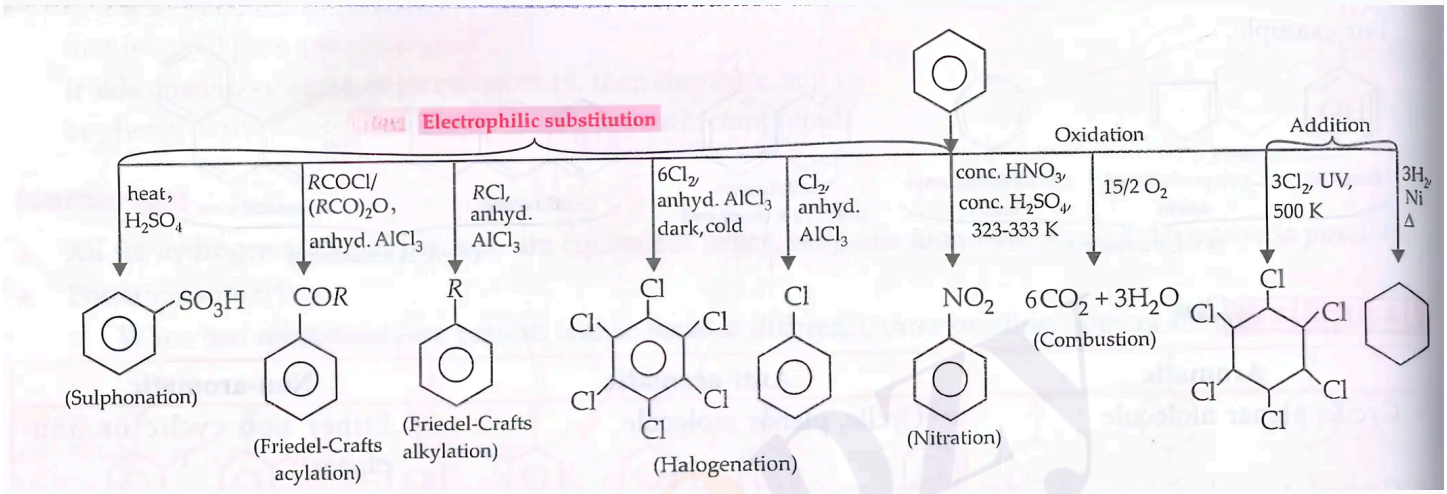
Memory Aids

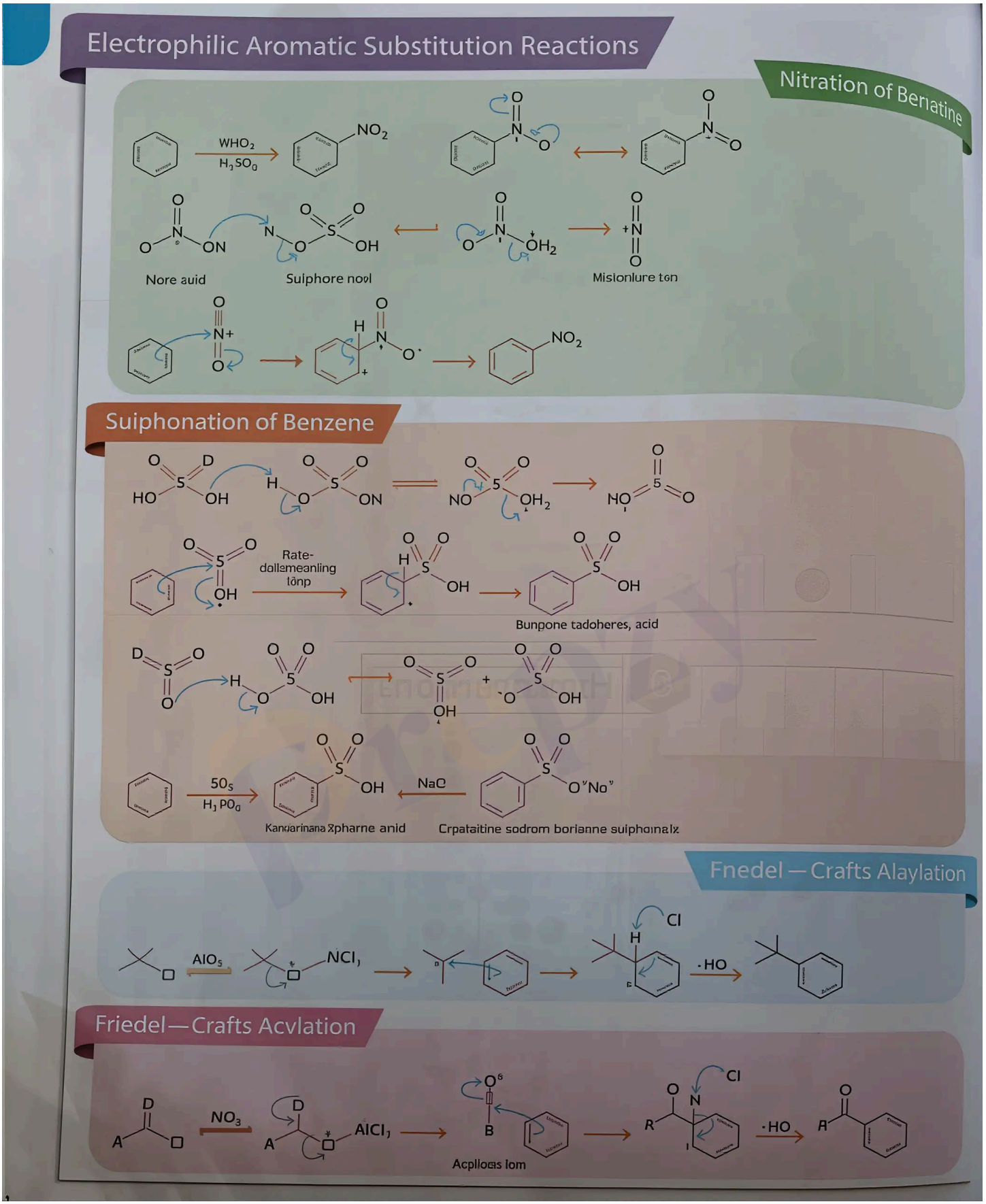
- Non-polar, aromatic smell, sooty flame.
- Boiling point ↑ with size; melting point depends on symmetry.

Chemical Properties

Reactivity

- Aromatic hydrocarbons are less reactive than alkenes/alkynes due to π-electron delocalisation.
- Undergo electrophilic substitution reactions (EAS) replacing H on benzene ring.
- Can undergo addition and oxidation under special conditions.





Solved Examples

- **Ex 1:** Name the product of nitration of benzene.
  Solution: Nitrobenzene (benzene with -NO_2 group).

- **Ex 2:** What catalyst is used in Friedel-Crafts alkylation?
  Solution: $AlCl_3$.

Practice Set

- Q1: Which reaction is typical for benzene?
  A. Addition B. Electrophilic substitution C. Free radical substitution D. Polymerisation
- Q2: Which reagent is used for sulphonation of benzene?
  A. HNO_3 B. H_2SO_4 C. SO_3 in H_2SO_4 D. $AlCl_3$
- Q3: Friedel-Crafts alkylation requires?
  A. RCl + $AlCl_3$ B. RCOCl + $AlCl_3$ C. HNO_3 + H_2SO_4 D. Cl_2 + $FeCl_3$

Answer Key

- Q1: B - Benzene undergoes electrophilic substitution.
- Q2: C - Sulphonation uses SO_3 in H_2SO_4.
- Q3: A - Friedel-Crafts alkylation uses alkyl halide and $AlCl_3$.

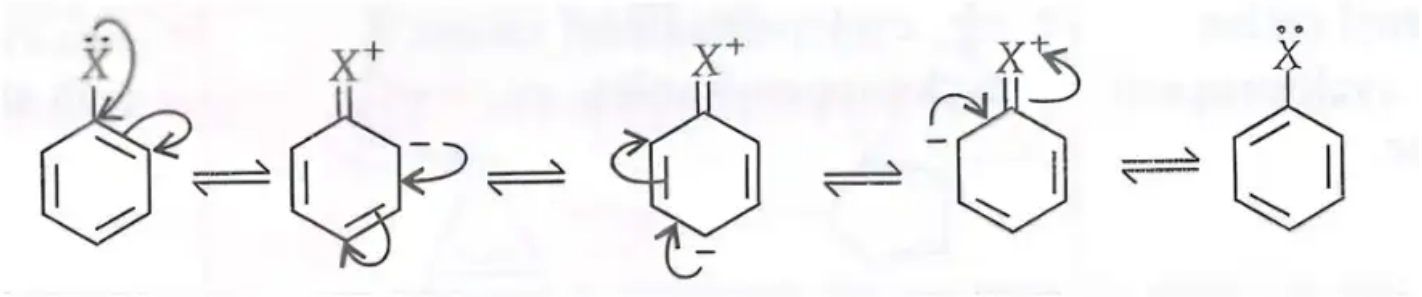
Memory Aids

- Benzene prefers substitution over addition due to π-electron stability.
- Common EAS: nitration, sulphonation, Friedel-Crafts alkylation/acylation.

Directive Influence of a Functional Group in Mono-Substituted Benzene

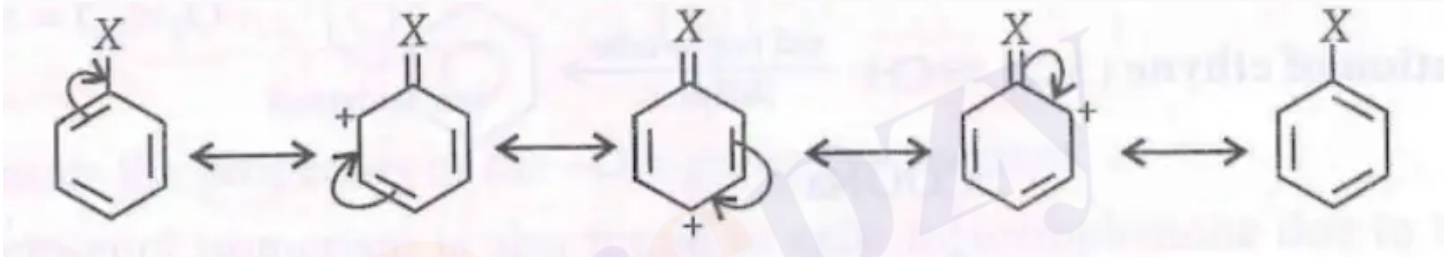
Ortho and Para Directing Groups

- Groups with +M effect increase electron density at ortho and para positions.
- Electrophiles attack electron-rich ortho and para positions.
- Examples: —CH_3, —C_2H_5, —OCH_3, —NH_2, —NHR, —$NHCOCH_3$, —OH, —F, —Cl, —Br, —I.



Meta Directing Groups

- Groups with -M effect decrease electron density at ortho and para positions.
- Electrophiles attack meta position.
- Examples: —NO_2, —CHO, —COR, —COOH, —COOR, —SO_3H, —CN.
- Halogens are ortho/para directing but deactivating.



Solved Examples

- **Ex 1:** Predict the major product when chlorobenzene undergoes nitration.
  Solution: Nitro group attaches at meta position due to -M effect of Cl.

Practice Set

- Q1: Which group directs electrophiles to ortho and para positions?
  A. —NO_2 B. —OH C. —COOH D. —CN
- Q2: Halogens are:
  A. Ortho/para directing and activating B. Meta directing and deactivating C. Ortho/para directing and deactivating D. Meta directing and activating
- Q3: Which group is meta directing?
  A. —NH_2 B. —CH_3 C. —NO_2 D. —OH

Answer Key

- Q1: B - —OH is ortho/para directing (+M effect).
- Q2: C - Halogens are ortho/para directing but deactivating.
- Q3: C - —NO_2 is meta directing (-M effect).

Memory Aids

- +M groups: activate ring, direct ortho/para.
- -M groups: deactivate ring, direct meta.
- Halogens: special case, ortho/para directing but deactivating.

Carcinogenicity and Toxicity

Overview

- Benzene and polynuclear hydrocarbons with more than two fused benzene rings are toxic and carcinogenic.
- These compounds form during incomplete combustion of organic materials like tobacco, coal, and petroleum.
- They enter the human body, undergo biochemical reactions, damage DNA, and cause cancer.

Solved Examples

- **Ex 1:** Identify a carcinogenic compound formed from incomplete combustion of coal.
  Answer: Benzo[a]pyrene (a polynuclear hydrocarbon with five fused benzene rings).

Practice Set

- **Q1:** Which of the following is a carcinogenic polynuclear hydrocarbon?
  A. Benzene
  B. Naphthalene

C. Benzo[a]pyrene
D. Toluene

- **Q2:** Polynuclear hydrocarbons are primarily formed by:
  A. Complete combustion of organic materials
  B. Incomplete combustion of organic materials
  C. Photosynthesis
  D. Electrolysis of water
- **Q3:** What is the primary biological effect of carcinogenic hydrocarbons?
  A. DNA repair
  B. DNA damage leading to cancer
  C. Protein synthesis
  D. Cell respiration

Answer Key

- **Q1:** C. Benzo[a]pyrene - It is a known carcinogenic polynuclear hydrocarbon formed during incomplete combustion.
- **Q2:** B. Incomplete combustion of organic materials - This process forms toxic polynuclear hydrocarbons.
- **Q3:** B. DNA damage leading to cancer - Carcinogens damage DNA causing mutations and cancer.

Memory Aids

- Polynuclear hydrocarbons = multiple fused benzene rings > 2 rings.
- Incomplete combustion = source of carcinogens like benzo[a]pyrene.
- Carcinogens damage DNA → cancer.